

Host and defect-related photoluminescence of structurally disordered $\text{K}_3\text{WO}_3\text{F}_3$ oxyfluoride crystals

A V Kozlov and V A Pustovarov

Ural Federal University, Mira str. 19, 620002 Yekaterinburg, Russia Russia

E-mail: KozlovArtemVladimirovich@gmail.com

Abstract. Spectra of photoluminescence (PL) in the region of 1.5–5.5 eV, PL excitation spectra (3–22 eV), PL decay kinetics and PL temperature dependence were measured for single crystals and ceramics $\text{K}_3\text{WO}_3\text{F}_3$ as well as for ceramics $\text{K}_3\text{WO}_3\text{F}_3$ irradiated by fast electrons. Synchrotron radiation was used for low temperature PL experiments with time resolution. Single crystals are transparent in microwave, visible and near UV range, inter-band transition energy is $E_g = 4.3$ eV. In $\text{K}_3\text{WO}_3\text{F}_3$, the wide band luminescence in the region of 2.5 eV with the Stokes shift of 1.5 eV with the microsecond decay kinetics is connected with luminescence of triplet self-trapped excitons (STE). This luminescence is formed by electronic transitions in $[\text{WO}_3\text{F}_3]$ octahedron. Different distortion of KWOF crystal lattice is manifested in the change of the Stokes shift of the STE luminescence band. The 3.2 eV emission band in low-temperature PL spectrum with decay times of 1.8 ns and 11 ns corresponds to singlet STE luminescence. A new 2.9 eV emission band is discovered in low-temperature PL spectrum in the samples irradiated by fast electrons ($E = 10$ MeV, $D = 160$ kGy). This emission band is excited not through the intracenter mechanism but through the creation of excitons bound on the defects. It is suggested that it is F-like centers of anionic sublattice induced by the mechanism of elastic collision.

1. Introduction

The group of crystals based on tungstates/molybdates have been of particular interest for over a hundred years. They are widely used in a great range of tasks: in laser technology, as scintillation materials in radiation safety systems, for thermal neutrons detection, double β -decay, etc. In particular, high purity crystals PbWO_4 are used as scintillation detectors in the Large Hadron Collider.

The group of oxyfluorides with general formula $\text{A}_3\text{MO}_3\text{F}_3$, where A can be rubidium, cesium, or potassium and M can be tungsten, titanium, niobium or molybdenum, are attractive compounds for developing new noncentrosymmetric crystals having ferroelectric and ferroelastic properties. This is achieved due to the strong distortion of metal-(O,F) polyhedra in the crystal lattice because of different ionicity of metal-O and metal-F bonds. The luminescence spectroscopy can be a sensitive method to study the character of lattice distortion of oxyfluorides.

However, nowadays there are almost no studies dedicated to the study of photoluminescence properties for this crystal group. In [1,2] such research of crystal $\text{K}_3\text{WO}_3\text{F}_3$ was initiated using standard laboratory equipment and time-resolved spectroscopy in a microsecond time range. Moreover, in crystals of this class, there has lately been discovered ultrafast intraband luminescence with a decay time of tens of picoseconds that may have a potential use, for example, in positron emission tomography [3].



The aim of this research is the study of luminescence properties of crystals $\text{K}_3\text{WO}_3\text{F}$ using the method of low-temperature time-resolved spectroscopy, identification of PL excitation mechanisms and defining the role of radiation induced defects of the crystal structure in the processes of energy transformation.

2. Experimental results and discussion

2.1. Samples and experimental details

Three different types of $\text{K}_3\text{WO}_3\text{F}_3$ samples were studied: single crystal, ceramics and ceramics irradiated by fast electrons (the energy of 10 MeV, dose $D = 160$ kGy). These samples were grown and characterised in the Institute of Geology and Mineralogy SB RAS (Novosibirsk, Russia). Methods of growing and attestation are thoroughly described in [4]. In this context, we will discuss only principal moments. Crystals were grown by the method of solid phase synthesis. Both Raman scattering and XRD methods were used in order to certificate crystals (figure 1 and figure 2). XRD method (figure 2) shows the presence of one pure monoclinic phase with structural parameters $a = 8.7459(2)$ Å, $b = 8.6930(4)$ Å, $c = 6.1650(3)$ Å, $\beta = 135.178(2)$. In Raman scattering spectrum (figure 1), two regions can be distinguished: the first one in the range from 750 to 1000 cm^{-1} corresponds to stretching vibrations of W–O ion bonds, the second region located under 650 cm^{-1} corresponds to stretching vibrations W–F. Except for the above mentioned certification methods, others were also used for particular chemical analysis. All of them confirmed the adequacy of samples to the monoclinic crystal structure of $\text{K}_3\text{WO}_3\text{F}_3$.

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured using a 400 W deuterium discharge lamp (DDS-400), two double prism DMR-4 type monochromators and a R6358-10 (Hamamatsu) type photomultiplier tube. The PLE spectra were normalized to an equal number of photons incident on the sample, using a yellow lumogene-luminophore with a unit quantum yield in the studied energy range. Under UV-VUV excitation using synchrotron radiation (SR), the time-resolved PL spectra, PL decay kinetics as well as PL excitation spectra were measured on a SUPERLUMI station (channel I, HASYLAB, DESY) [5]. The measurements of PL spectra were carried out using an ARC Spectra Pro–308i monochromator and R6358P Hamamatsu photomultiplier tube. The PL spectra were recorded in two time windows – fast component: a delay relative to the start of the exciting SR-pulse $\delta t_1 = 0.6$ ns, span of time windows $\Delta t_1 = 6.0$ ns; – slow component: $\delta t_2 = 32$ ns, $\Delta t_2 = 48$ ns. The time resolution of the entire detection system was 1 ns (FWHM). The temporary interval between excitation SR pulses was equal to 96 ns. The PL excitation spectra were corrected to an equal number of photons incident on the sample recorded using sodium salicylate.

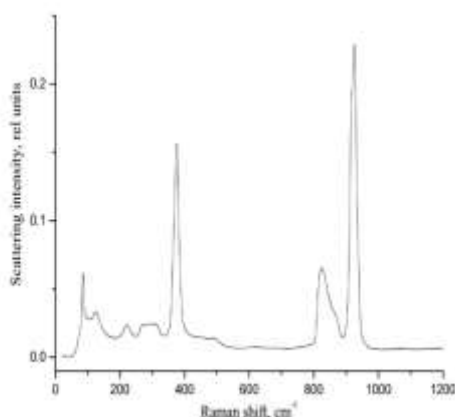


Figure 1. The Raman scattering spectrum of $\text{K}_3\text{WO}_3\text{F}_3$ crystal according to [4, 5].

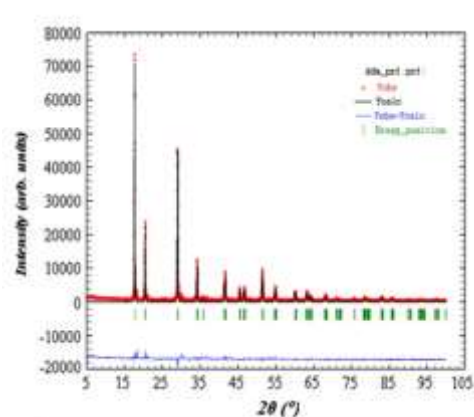


Figure 2. The XRD analysis of $\text{K}_3\text{WO}_3\text{F}_3$ crystal according to [4, 5].

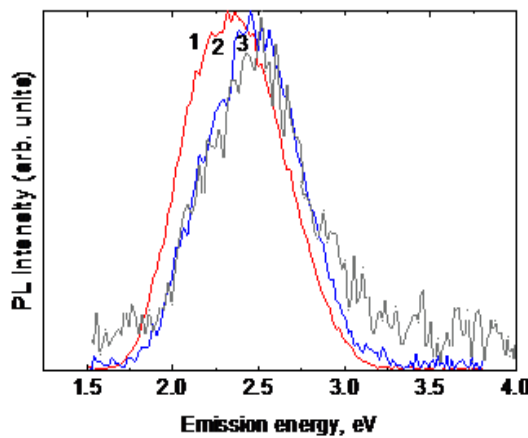


Figure 3. The normalized PL spectra of $K_3WO_3F_3$ at $T = 295$ K. Excitation energy = 4.11 (1), 4.70 (2) and 5.18 eV (3).

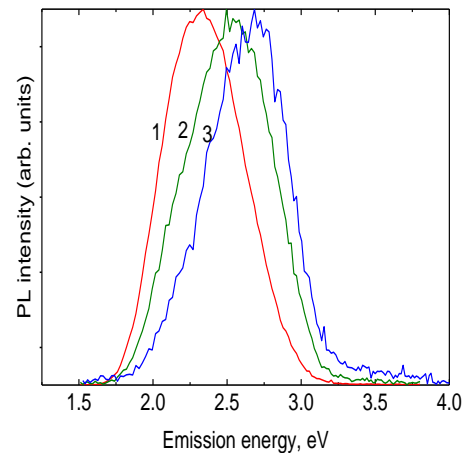


Figure 4. The normalized PL spectra of $K_3WO_3F_3$ at $T = 90$ K. Excitation energy = 4.11 (1), 4.70 (2) and 5.18 eV (3).

2.2. Luminescence spectroscopy data and discussion

It should be noted that during sample studying there were discovered no significant differences between ceramics and a single crystal $K_3WO_3F_3$. In this connection, in the description of the obtained results, there will be data for ceramics, and in case there are some differences with the single crystal, it will be specified separately.

In figure 3 and figure 4, the normalized PL spectra of $K_3WO_3F_3$, measured using a D_2 discharge lamp at room temperature and $T = 90$ K under different excitation energy E_{exc} are shown. A broad band in the region of 2.2–2.6 eV characterizes these PL spectra, and its maximum depends on the energy of the excited photons E_{exc} . This broad band emission can be effectively excited only in the long-wave edge of fundamental absorption or in the region of interband transitions. (Recall that the minimum energy of the interband transitions is $E_g = 4.3$ eV at the room temperature in $K_3WO_3F_3$, according to the data in [5]). This emission is not excited in the region of crystal transparency (figure 5 and figure 6). Moreover, the band of 4.2 eV in the PL excitation spectrum is shifted in the direction of higher energies together with the fundamental absorption edge when crystal temperature drops. Such behavior of the photoluminescence is typical of intrinsic luminescence in tungstate or molybdate crystals. The intrinsic luminescence of tungstates is usually ascribed to the radiative relaxation of exciton-like excitations localized on WO_6 octahedra or WO_4 tetrahedra [7]. However, in KWO₃F₃, the PL maximum position depends on the energy of the excited photons E_{exc} . This fact points that at different exciting energies luminescence appears due to electronic transitions in WO_3F_3 octahedron with various local distortions. Based on all above mentioned properties and by analogy with the tungstates crystals, we can say that the photoluminescence in $K_3WO_3F_3$ is associated with the luminescence of self-trapped excitons, i.e. it is not connected with the point defects of crystal structure or an impurity center.

Normalized excitation spectrum recorded in a wide range of energies from 3 to 22 eV at temperature 8.8 K for two emission energies 2.42 eV and 3.20 eV using synchrotron radiation is shown in figure 6. It is seen that the main excitation band is on the edge of the fundamental absorption, next in the region of higher energies (vacuum ultraviolet region), efficiency of excitation is low. It means inefficiency of conditioning transport of charge carries and presence of competing channels of capture with the following nonradiative recombination on the defects or crystal surface.

Photoluminescence spectra measured with time-resolution at $T = 8.8$ K are presented in figure 7. Using decay kinetics, there were distinguished a fast component – red curve, a slow component – green curve and a time integrated component – black curve.

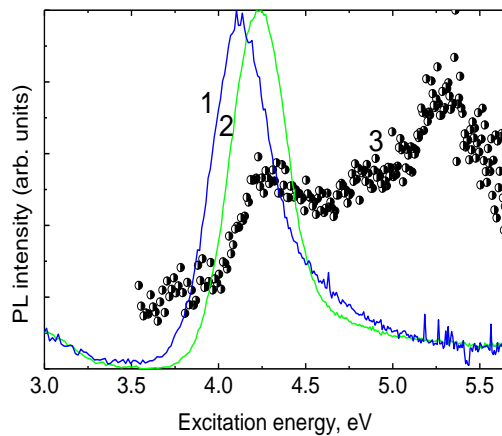


Figure 5. The normalized PL excitation spectra of $\text{K}_3\text{WO}_3\text{F}_3$ measured using a D_2 discharge lamp, $T = 295$ (1) and 90 K (2, 3). Emission energy $E_{\text{emis}} = 2.42$ (1, 2) and 3.20 eV (3).

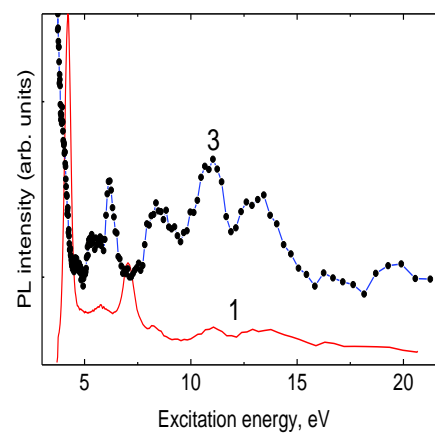


Figure 6. The normalized PL excitation spectra of $\text{K}_3\text{WO}_3\text{F}_3$ measured using synchrotron radiation, $T = 8.8$ K. Emission energy $E_{\text{emis}} = 2.42$ (1) and 3.20 eV (2).

The parameters of time windows are mentioned in the previous section, furthermore, they are shown in figure 8. The fast component shows well the presence of band 3.2 eV, which previously did not manifest itself in the PL spectra due to low intensity in contrast to the wide band 2.4 eV. As seen in Fig. 3, their band 3.2 eV is well excited by energy 4.2 eV, as well as by energy 5.2 eV. The PL decay kinetics allows us to assume singlet nature of that band. In contrast to the main band 2.4 eV where the decay time is a few tens of microseconds, the 3.2 eV band is characterised by the decay time in the nanosecond region.

Let us discuss more thoroughly excitation mechanisms of luminescence. When excited, there is a high probability of electronic radiative transition from the triplet level to the ground state. However, such transition is prohibited by the selection rules, and as a result, the decay time is a few tens of microseconds. In case when an electron in the excited exciton is on the singlet level, the selection rules allows making a radiative transition to the ground state, the decay kinetics is thousands of times faster in this case. To assess the life time of an exciton in the singlet state, approximation of two exponential was carried out, the results are $\tau_1 = 1.8$ ns и $\tau_2 = 11$ ns. As we suppose, the presence of two different τ values may caused by the distortion of the crystal structure and, as a consequence, by different local surroundings near emission centers.

Further $\text{K}_3\text{WO}_3\text{F}_3$ irradiated by fast electrons was studied. Irradiation by fast electrons involves the creation of point defects due to elastic displacement that will supposedly lead to the creation of capture centers of charge carriers. Such defects affect the intrinsic luminescence and new defect-related luminescence can appear. To evaluate changes in the irradiated crystal, PL emission and PL excitation spectra were measured at the conditions similar to those for the previously unirradiated crystal (figure 4 and figure 5, respectively). At room temperature, no changes were revealed regarding the unirradiated crystal. However, at low temperature, a new emission band in PL spectrum appeared (figure 9, curve 1).

The excitation spectrum of the new PL emission band is presented in figure 10. A new PL band is effectively excited in the region of 4.25 and 5.2 eV. As in case with the unirradiated crystal, a low energy band corresponds to the long-wave edge of the fundamental absorption, i.e. to creation of excitons. It should be noted that the new emission band is not excited in the crystal transparency below 4.0 eV. This allows us to conclude that the new band is excited not through the intracenter mechanism but by the creation of excitons bound on defect. We assume that it is F-like centers of anionic

sublattice induced by the mechanism of elastic collision. However, this assumption needs further studies.

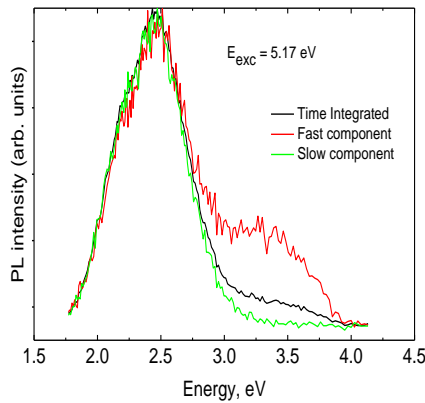


Figure 7. Time-resolved PL spectra of $K_3WO_3F_3$ measured at $T=8.8$ K.

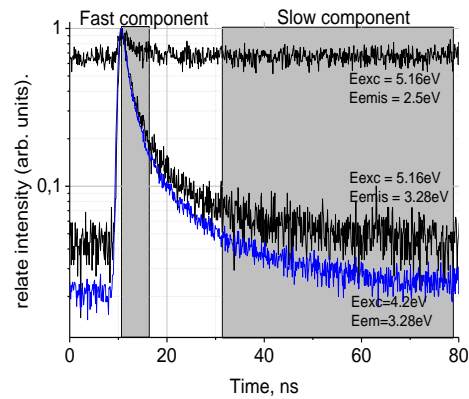


Figure 8. Decay kinetics of $K_3WO_3F_3$ measured at $T=8.8$ K. Positions of time windows (fast component and slow component) are shown.

The temperature dependence of PL intensity for crystals reference and irradiated by fast electrons is shown in figure. 11. All temperature dependencies are recorded from the temperature 90 K to 400 K. Before irradiation, the temperature dependence in the main band is well described by Mott's law. The quenching starts from $T = 150$ K, the activation energy is 0.20 eV. However, after irradiation (figure. 11 (2)), it significantly changes and no longer obeys Mott's law. The quenching starts immediately from $T = 90$ K that indicates the influence created by the irradiation defects to the main band. The 2.9 eV emission band in the PL spectra of the irradiated crystal in its turn has absolutely different temperature dependence, where the process of luminescence quenching starts right from $T = 90$ K. The activation energy is approximately 0.10 eV. However, the measurements at lower temperatures are needed to examine this temperature dependence in detail.

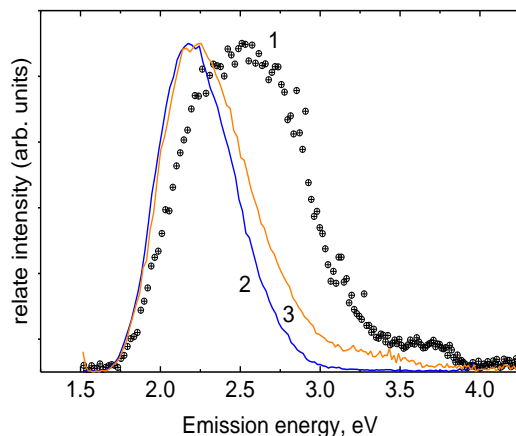


Figure 9. The normalized PL spectra of $K_3WO_3F_3$ irradiated by fast electrons. Excitation energy = 5.2 (1), 4.2 (2) and 4.7 eV (3).

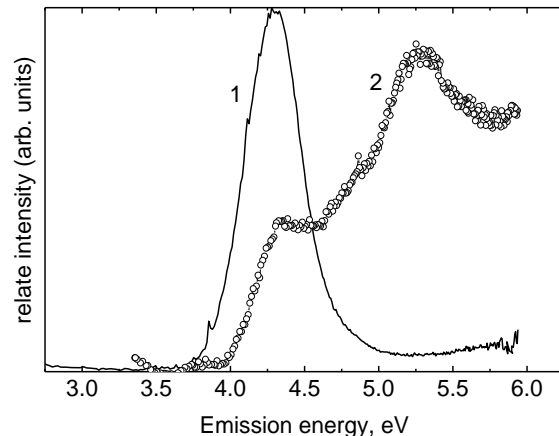


Figure 10. The normalized PL excitation spectra of $K_3WO_3F_3$ irradiated by fast electrons. Emission energy = 2.5 (1) and 2.9 eV (2), $T = 90$ K.

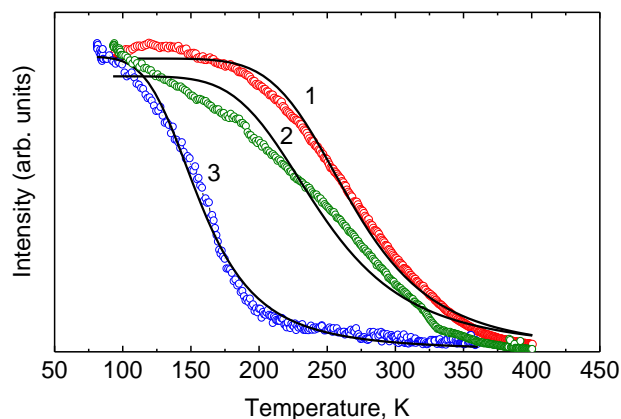


Figure 11. The temperature dependence of PL yield of reference (1) and irradiated by fast electrons (2, 3) $\text{K}_3\text{WO}_3\text{F}_3$ ceramics. $E_{\text{exc}} = 4.2$ eV, $E_{\text{mis}} = 2.5$ eV (1, 2); $E_{\text{exc}} = 5.08$ eV, $E_{\text{mis}} = 2.9$ eV (3). A thin line represents an approximation using the Mott's law, the activation energy shown in figures.

Thus, the PL data show that after irradiation by fast electrons new point defects are formed in the crystal structure. They affect the intrinsic luminescence and create new PL centers at low temperature.

3. Conclusions

The broad band luminescence in the region of 2.5 eV with the Stokes shift of ~ 1.5 eV with the microsecond decay kinetics in $\text{K}_3\text{WO}_3\text{F}_3$ crystals is connected with its intrinsic luminescence – luminescence of STE from the excited triplet states. This luminescence is formed by electronic transitions in $[\text{WO}_3\text{F}_3]$ octahedron. Different distortion of $\text{K}_3\text{WO}_3\text{F}_3$ crystal lattice is manifested in the change of the Stokes shift of luminescence band of self-trapped excitons.

The 3.2 eV emission band in low-temperature PL spectrum with decay time of 1.8 ns corresponds to electronic transitions from the singlet excited state of STE. Under interband excitation, the PL yield is low that points to ineffective transport of charge carriers due to the competition of non-radiative recombination on point defects.

A new 2.9 eV emission band is discovered in low-temperature PL spectrum in the samples irradiated by fast electrons. This emission band is excited not through the intracenter mechanism but through the creation of excitons bound on defects. It is suggested that it is F-like centers of anionic sublattice induced by the mechanism of elastic collision.

Acknowledgments

Authors are grateful to Dr. L.I. Isaenko for the provided samples. This work has been supported by the Ministry of Education and Science of the Russian Federation (the basic part of the government mandate) as well as by Act 211 Government of the Russian Federation (contract #02.A03.21.0006), Center of Excellence “Radiation and Nuclear Technologies”.

References

- [1] Omelkov S I, Spassky D A, Pustovarov V A, Kozlov A V and Isaenko L I 2016 *Optical Materials* **58** pp 285–289
- [2] Kozlov A V and Pustovarov V A 2016 AIP Conference Proceedings **1767** 020037
- [3] Omelkov S I, Nagirnyi V, Vasil'ev A N and Kirm M 2016 *J. of Luminescence* **176** pp 309–317
- [4] Molokeev M S, Misyl S V, Fokina V D, Kocharova A G and Aleksandrov K S 2011 *Physics of the Solid State* **53** pp 834–839
- [5] Atuchin V V, Isaenko L I, Kesler V G, Lin Z S, Molokeev M S, Yelissev A P and Zhurkov S A 2012 *J. of Solid State Chemistry* **187** pp 159–164
- [6] Zimmerer G 2007 *Radiation Measurements* **42** pp 859–864
- [7] Zhang Y, Holzwarth N A W and Williams R T 1998 *Physical Review B* **57** 12738–50